5.6 Secondary Ion Mass Spectroscopy Analysis

Technology Need

DOE has many contamination problems requiring the determination of contaminants that adhere tightly to waste, environmental, and industrial surfaces. There is a critical need in DOE and industry for characterization technologies that are fast, inexpensive, and can address surface contamination. An excellent example of this need is the detection of mercury on soil samples, and equally important, the identification of mercury species present. The mercury speciation issue is important because differing environmental mobility among the species alters risk assessment associated with mercury contamination. For example, mercury present as $Hg(NO_2)_3$ is highly mobile and would require containment; on the other hand, mercury present as HgO strongly adsorbs to soil and poses a much lower risk. At the present time, there is no facile means to make a distinction between these species on soil samples. See Figure 5.6-1.

Another example of this need is characterization of core and particulate samples from radioactive waste in underground storage tanks, which currently costs an average of $750,000/core analysis. Technologies capable of determining chemical speciation are needed to reduce the number of analyses needed, and to improve the estimation of tank energy content (critical for risk assessment associated with tank characterization and remediation activities).

Figure 5.6-1 Depiction of SIMS Bombardment of Hg-Contaminated Soil

Technology Description

Fast, inexpensive, and non-polluting instrumentation for the detection of surface contaminants is being developed at the Idaho National Engineering Laboratory (INEL) using advanced Secondary Ion Mass Spectroscopy (SIMS) technology. The attributes of this technology make it extremely attractive for waste and environmental characterization:

- No sample preparation is required
- No waste is generated

- Analysis is rapid and simple
- Capable of speciation, "fingerprinting"
- Amenable to almost any sample type
- Amenable to involatile organics, salts

SIMS has a simple principle of operation: surfaces are bombarded with high-energy particles, which "sputter" the contaminants into the gas-phase, where they can be detected as ions.

The objective of the SIMS analysis program is to develop instrumentation and chemical applications for the detection of chemical species, identification of semivolatile, involatile, or adsorbed contaminants on the surfaces of soils, minerals, salts, rocks, and other difficult to handle sample types. During the course of the SIMS analysis program, detection applications and instrument development were accomplished. In FY96, the objective of the program is to transfer technology to end users and to instrument manufacturers.

Benefits

New analytical capability, reduced analysis cost, and technology transfer are among the benefits of the SIMS Demonstration Program. Since the technology requires no sample preparation, is rapid, and generates no waste, lower analytical cost can be realized. The technology also provides a facile approach toward the analysis of involatile contaminants, which are difficult to analyze using current methods and instrumentation: organophosphate and hazardous metal species are examples of classes of chemicals which are amenable to the SIMS characterization approach. The program has also resulted in the transfer of software components to instrument manufacturers, and the transfer of hardware components is expected in the near future. The development of the transportable ion trap SIMS instrument has resulted in a device which can be used in the field for on-site characterizations. Instruments that are based on the OTD-funded prototype are being constructed for other government users.

Collaboration/Technology Transfer

Technology transfer has been pursued with three vendors. Given the nature of the technology, the focus of the technology transfer activities has been on transfer of SIMS components, instead of a complete instrumental package, which would require the manufacturer to engineer it's instrument from scratch. A license was completed for data acquisition and instrument control software with Extrel (Pittsburgh, PA). Transfer of the primary ion gun technology to Phi-Evans, Inc. (Redwood City, CA) has been actively pursued. This activity requires a head-to-head comparison of existing ion guns with the INEL $Re0_4$-

gun. It is expected that this activity will be completed by May 1996, where upon negotiations for transfer of ion gun technology will be renewed with Phi-Evans.

Figure 5.6-2 is a schematic diagram of a prototype ion trap SIMS instrument being developed at INEL. The instrument is capable of anion and cation acquisitions, and enhanced selectivity and sensitivity will result from MS/MS and selective ion storage capability. The capability of the instrument has resulted in a DOD end user (U.S. Army Chemical Material Destruction Agency, Non-Stockpile Program), who is funding fabrication of second generation prototype ion trap SIMS instruments. This development has motivated negotiations with Teledyne (Mountain View, CA, an ion trap vendor), for the purpose of transferring SIMS components, thereby providing the end user with a commercial technology vendor.

Accomplishments

The rapid analysis of simulated salt cake samples was demonstrated using the laboratory-based SIMS instrument located at the INEL. The analyses required no sample preparation, and hence required less than 10 minutes; in addition, no waste was generated. A unique attribute of our R&D 100 Award-winning, pulsed-extraction SIMS instrument is the ability to analyze cations and anions at the same time. This attribute is especially valuable for salt cake analyses because the salt samples contain both anion and cation species. Nitrite, nitrate, cyanide, and hydroxide anions, and iron, sodium, potassium, and nickel complexes were detected.

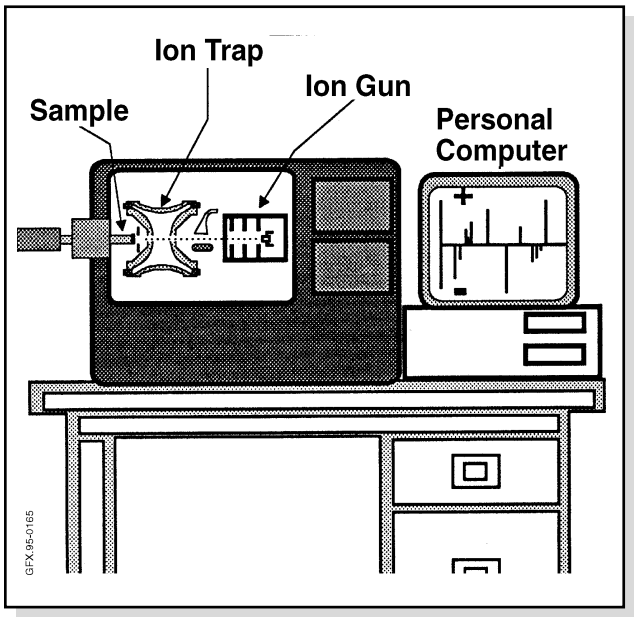

Figure 5.6-2 Schematic diagram of prototype ion trap SIMS instrument being developed at INEL.

Since demonstrating SIMS for the characterization of salt cake, the SIMS analysis has been redirected toward the determination of metal speciation on soil samples. Research conducted in FY95 using SIMS showed that different mercury species could be distinguished by forming surface derivatives, which is easily accomplished using simple organic acids and bases. The mercury surface derivatives were specific for the inorganic mercury species originally present, and were easily detected using an ion trap SIMS instrument (see Figure 5.6-2).

Instrument transportability, and improved sensitivity and selectivity are desired attributes of the instrumentation that will be constructed in this program. An ion trap mass spectrometer (ITMS) satisfies these requirements, and therefore an ion trap SIMS instrument was constructed in FY95. Using this instrument, it is possible to observe fragile, but species-diagnostic organometallic ions, which cannot be observed using other types of instrumentation. The instrument is also smaller in size: the current version resides on a cart which has a footprint of approximately 2 x 3 feet.

TTP Information

Secondary Ion-Mass Spectroscopy Analysis technology development activities are funded under the following Technical Task Plan (TTP):

TTP No. ID72C241 "Secondary Ion-Mass Spectroscopy Analysis"

Contacts

James E. Delmore
Principal Investigator
Idaho National Engineering Laboratory
P.O. Box 1625
Idaho Falls, ID 83415-2208
(208) 526-2820

Tom Williams
Technical Program Officer
U.S. Department of Energy
Idaho Operations Office
Idaho Falls, ID 83415
(208) 526-2460

Bibliography of Key Publications

Groenewold, G.S., J.C. Ingram, J.E. Delmore, and A.D. Appelhans. "Static SIMS Analysis Of Tributyl Phosphate On Mineral Surfaces: Effect Of Fe(II)," *Journal of American Soc. Mass Spectrometry*, p. 6, 165-74 (1995).

Groenewold, G.S., J.C. Ingram, J.E. Delmore, A.D. Appelhans, and D.A. Dahl. "Rapid Detection of Tri-n-butyl Phosphate on Environmental Surfaces Using Static SIMS," *Journal of Hazardous Materials*, p. 41, 359-70 (1995).

Groenewold, G.S., A.D. Appelhans, J.C. Ingram, J.E. Delmore, and D.A. Dahl. "Surface Derivatization of Inorganic Mercury: Formation of bis(Ankylamine) Mercury Cations," *Journal of American Chemical Society*, submitted (1996).